Development of Nickel-based Nanoparticle Catalysts toward Efficient Water Splitting(Abstract_要旨)

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論文題目	Development of Nickel-based Nanoparticle Catalysts toward Efficient Water Splitting （高効率水分解のためのニッケル化合物ナノ粒子触媒の開発）		

（論文内容の要旨）

Chapter 1: General Introduction

In recent decades, there has been a continuous need to replace fossil fuels with environmental-friendly and sustainable alternative energy sources. One of the attractive solutions would be the photoenergy conversion from sunlight to high-value-added chemicals like hydrogen gas by the photocatalytic reaction. Recently, the Ni-based electrocatalysts gained attention for high activity due to similar chemical properties, compared with the same group element, Pt, in the periodic table. Although the Ni-based electrocatalyst system has showed low onset potential and overpotential for water splitting, they have a practical limit associated with bulk like morphologies. The catalytic system based on nanoparticles (NPs) is one of the promising methodologies owing to their large specific surface areas. In addition, homogeneous dispersion of catalyst nanocrystals in solvent can be used to modify the various electrodes and photocatalysts by simple deposition or coating methods.

In this thesis, the author has investigated the selective synthesis of monodisperse NPs (spinel Ni_3S_4, heterostructured cubic-spinel $Cu_{2-x}Se$-Ni_3Se_4, spine Ni_3Se_4, and phase-segregated NiP_x@FeP_yO_z core@shell) and systematically demonstrated their electrocatalytic and photocatalytic activities for hydrogen and oxygen evolution reactions.

Chapter 2: Formation of Layer-by-Layer Assembled Cocatalyst Films of S^{2-}-Stabilized Ni_3S_4 Nanoparticles for Hydrogen Evolution Reaction

Metal sulfide NPs are potential candidates for water splitting cocatalysts, although their poor electrocatalytic activities, owing to the insulating surface ligands, is an obstacle to the practical use. In this work, the author selectively synthesized oleylamine (OLAm)-stabilized Ni_3S_4 (Ni_3S_4/OLAm) NPs by a hot-injection method. After the ligand exchange of the insulating ligands with S^{2-}, the Ni_3S_4 NPs were loaded on electrodes by a layer-by-layer assembly method with several kinds of metal cation linkers (Cd^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+}). The enhanced catalytic properties were confirmed by electrochemical measurements. A layer-by-layer assembled film with Ni^{2+} (11 cycles) showed an overpotential of 555 mV@–4mA/cm^2 at pH 6.8 and a higher and stable current density for 12 h. The catalytic activation was attributed to the structural transformation of Ni_3S_4 into $Ni(PO_x)_y$ during the hydrogen evolution, which contributed to the high and stable (photo)current densities of the layer-by-layer assembled films. In addition, when this layer-by-layer assembly method was applied to the CdS/Cu(In,Ga)Se_2 photocatalyst electrode, the resulting photoelectrode showed an enhanced photocurrent, compared with those of the Ni_3S_4/OLAm NPs-spin coated and bare photoelectrodes. These results indicate the versatility of layer-by-layer assembly for fabrication of ligand-free NP electrocatalyst films.

Chapter 3: First Chemical Synthesis of Spinel Ni_3Se_4 and Janus $Cu_{2-x}Se$-Ni_3Se_4

Nanoparticles with Excellent Catalytic Activity for Oxygen Evolution

The cation exchange reaction is an emerging area in NP research, because the substitution of original cations with different ones enables us to synthesize metastable NPs that could not be accessible by one-pot synthesis. In this work, by using cubic berzelianite $Cu_{2-x}Se$ NPs as a starting template, the author succeeded to replace Cu^{+} with Ni^{2+} to give the spinel Ni_3Se_4 phase and finely tune the molar ratio of Ni:Cu in NPs. The important points of the work are as follows. Firstly, the metastable spinel Ni_3Se_4 NPs were obtained by the cation exchange reaction, because both $Cu_{2-x}Se$ and spinel Ni_3Se_4 phases have the similar face centered cubic Se^{2-} sub-lattice, which enables to form the spinel Ni_3Se_4 phase with retention of Se^{2-} framework. Secondly, partially cation exchanged NPs showed Janus-type heterostructures composed of cubic $Cu_{2-x}Se$ and spinel Ni_3Se_4 phases due to the large lattice mismatch and immiscibility between these two phases. Thirdly, the Ni cation exchanged $Cu_{2-x}Se$ NPs showed large active sites and low charge transfer resistance, leading to efficient electrocatalytic activity. Especially, the $Cu_{2-x}Se$-Ni_3Se_4 NPs exhibited a lower overpotential of 230 mV@10 mA/cm^2 in 0.1 M KOH than the $Cu_{2-x}Se$ (568 mV@10 mA/cm^2) and Ni_3Se_4 NPs (250 mV@10 mA/cm^2). Our work not only provides a synthetic pathway to the novel phased NPs but also expands the modulating method to form high-performance energy conversion catalysts.

Chapter 4: Phase-segregated NiP_x@FeP_yO_z Core@shell Nanoparticles: Ready-to-use Nanocatalysts for Electro- and Photo-catalytic Water Oxidation through In-situ Activation by Structural Transformation and Spontaneous Ligand Removal

The high overpotential of the oxygen evolution reaction (OER) is a critical issue to be overcome to realize efficient overall water splitting and enable hydrogen generation by sunlight. Homogeneous and stable NPs dispersed in solvents are useful as both electrocatalysts and cocatalysts of photocatalysts for the electro- and photo-catalytic OER, respectively, through their adsorption on various electrode substrates. In this work, phase-segregated NiP_x@FeP_yO_z core@shell NPs are selectively synthesized by the reaction of $Fe(CO)_5$ with amorphous NiP_x seed-NPs. The NiP_x@FeP_yO_z NPs on conductive substrates exhibited higher electrocatalytic activity in the OER than those of other metal phosphide-based catalysts. The NiP_x@FeP_yO_z NPs can be also used and a cocatalyst of an anodic $BiVO_4$ photocatalyst to boost the photocatalytic OER. The excellent catalytic activity and high stability of the NiP_x@FeP_yO_z NPs without any post-treatments are derived from in situ activation through both the structural transformation of NiP_x@FeP_yO_z into mixed hydroxide species, (Ni, Fe)O_xH_y, and the spontaneous removal of the insulating organic ligands from NPs to form a smooth and robust (Ni, Fe)O_xH_y substrate heterointerface during the OER.

Chapter 5: Conclusions

The author attempted to achieve the control over novel crystal structure and morphology of NPs and apply them to solar energy conversion. The author revealed that the photo-energy conversion properties of NPs are dependent on their surface capping agents, and provided a new pathway to highly active energy conversion system for sustainable future of human beings.

（続紙　２　）

（論文審査の結果の要旨）

金成元氏は、可視光水分解光触媒の助触媒として、触媒活性の高い Pt と同族の Ni に着目し、種々の Ni 化合物ナノ粒子の合成、ならびに、その電極触媒特性および光触媒特性について検討した。まず、オレイルアミンに保護された導電性 Ni_3S_4ナノ粒子の合成に世界で初めて成功するとともに、S^{2-}への配位子交換が進行することを明らかにした。また、S^{2-}に保護された Ni_3S_4ナノ粒子を種々の金属イオンにより架橋集積した Ni_3S_4ナノ粒子膜が、水素生成電極触媒として 555 mV@–4mA/cm^2（Ni^{2+}、pH 6.8）の過電圧を 12 時間程度安定に示すこと、CdS/Cu(In,Ga)Se_2光触媒の助触媒としても高活性を示すことを実証し、触媒活性種が $Ni(PO_x)_y$であることを明らかにした。次に、酸素生成助触媒としてこれまでに合成例のない準安定スピネル Ni_3Se_4相に着目し、$Cu_{2-x}Se$ ナノ粒子のカチオン交換による Ni_3Se_4ナノ粒子および $Cu_{2-x}Se$-Ni_3Se_4ヘテロ構造ナノ粒子の合成、ならびに、酸素生成電極触媒特性について検討した。その結果、酸素生成電極触媒特性において、$Cu_{2-x}Se$-Ni_3Se_4ヘテロ構造ナノ粒子が $Cu_{2-x}Se$（568 mV@10 mA/cm^2 in 0.1 M KOH）あるいは Ni_3Se_4ナノ粒子（250 mV@10 mA/cm^2）よりも低い過電圧（230 mV@10 mA/cm^2）を示すことが明らかとなり、カチオン交換反応が新規助触媒創製に有用な手法であることを明らかにした。

一方、金成元氏は、Ni 化合物を基盤とする新規酸素生成助触媒として、NiP_x@FeP_yO_zコアシェルナノ粒子の合成に成功した。NiP_x@FeP_yO_zコアシェルナノ粒子の酸素生成電極触媒特性は、他の金属リン化物ナノ粒子よりも優れていることを明らかにした。また、NiP_x@FeP_yO_zコアシェルナノ粒子 $BiVO_4$光触媒に担持することにより、光触媒活性の増加および光触媒安定性の向上を達成した。さらに、活性種が$(Ni, Fe)O_xH_y$であり、表面配位子が自発的に除去されることを明らかにし、可視光応答酸素生成光触媒の触媒特性向上に関して重要な知見を与えた。

よって、本論文は博士（理学）の学位論文として価値あるものと認める。また、平成３１年１月１８日、論文内容とそれに関連した事項について試問を行った結果、合格と認めた。

なお、本論文は、京都大学学位規程第１４条第２項に該当するものと判断し、公表に際しては、当該論文の全文に代えてその内容を要約したものとすることを認める。

要旨公表可能日：　　年　　月　　日以降